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IN PITS AND FISSURES OF TEETH FOR USE IN PREVENTIVE DENTISTRY
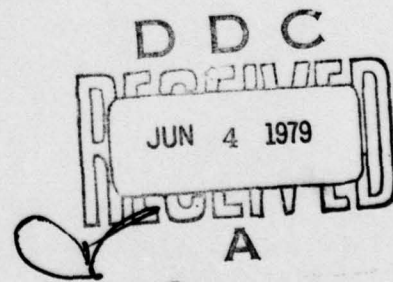
THOMAS J. O'KEEFE

AUGUST 1978

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U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND

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Further studies were undertaken to test the feasibility of using metal films, deposited by electroless or chemical means, for use in the military dental program.

The research effort during the past year was concentrated in the following areas: evaluation of the effects of preliminary treatments on the quality of metal plating, the use of alternate or additional etching agents, the testing of alternate reducing agents (other than hydrazine and ferrous sulfate), and morphological and rate studies of the deposited silver films.

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ABSTRACT

Further studies were undertaken to test the feasibility of using metal films, deposited by electroless or chemical means, for use in the military dental program.

The research effort during the past year was concentrated in the following areas: evaluation of the effects of preliminary treatments on the quality of metal plating, the use of alternate or additional etching agents, the testing of alternate reducing agents (other than hydrazine and ferrous sulfate), and morphological and rate studies of the deposited silver films.

I. INTRODUCTION

From the previous work it has been demonstrated that a thin metal film could be deposited successfully in vitro on extracted human teeth as well as in vivo on animals. All animal studies were conducted at the USAIDR Laboratories. Initially, the films were obtained using hydrazine as the reducing agent and these appeared to perform satisfactorily. Due to possible toxicity problems with hydrazine an alternate reagent, ferrous sulfate, was investigated. The data were encouraging but the results obtained were felt to be inferior to those obtained with hydrazine. As a result, the goals for the last year's work were to find more suitable reducing agents which produced deposits approaching those of hydrazine, to attempt to improve upon the ferrous sulfate system by chemical alterations to the system and to evaluate the possible effects of preliminary treatment of teeth prior to plating. Morphological, kinetic and phase identification studies were made to characterize the resultant metal deposits.

II. EXPERIMENTAL RESULTS

A. Preliminary Treatment of Teeth

Experiments were conducted to determine the effects of various treatments to the tooth surface prior to plating.

It was noted that the quality of the deposits was a function of the solutions used to store them, and Table I summarizes some of these results. There was less influence when hydrazine was used with AgF, but glycerine produced better conductivities than formaldehyde in general. Soaking in 0.9% saline solution before etching was also ineffective. Sodium bicarbonate was also found to be preferable to

TABLE I

Average resistance (Ω) of Ag plated enamel as a function of the tooth storage solution. The sequence of operation was: glycerin or formaldehyde, water wash and paper blot (WB), 42.5% H_3PO_4 etch for 60 sec., Ag^+ solution - reducing agent (5 X).

System	Glycerin Ω	Formaldehyde Ω
100 gpl AgF (pH = 6 with HNO_3) - 10 mlpl N_2H_4 (pH = 9.4)	17	36
100 gpl AgF (pH = 8.4 with NH_4OH) - 10 mlpl N_2H_4 (pH = 9.4)	9.7	9.2
100 gpl AgF (pH = 6 with HNO_3) - 400 gpl $FeSO_4.7H_2O$ (pH = 5.5 with NH_4OH)	98	5.7×10^4
100 gpl $AgNO_3$ (pH = 10 with NH_4OH) - 10 mlpl N_2H_4 (pH = 9.4)	35	8.0×10^4

TABLE II

Average resistance of Ag plated tooth enamel as a function of the etching agent and pH of the AgF solution. Sequence of operation was: glycerin or formaldehyde storage, Sparkleen scrub, 0 9% saline, WB, etchant for 60 sec., WB, 100 gpl AgF (HNO_3 or NH_4OH used to adjust pH) - 10 mlpl N_2H_4 (5 X).

Storage Solution	pH of AgF Solution	Etchant		
		42.5% H_3PO_4	21.25% H_3PO_4	1.0 M HCl
		Resistance (Ω)		
Formaldehyde	1.5	4.6×10^5	4.6×10^4	1.4×10^4
Glycerin	2.8	21	8.0	36
Glycerin	6.8	38	1.6×10^3	7.6×10^3
Glycerin	10.0	25	13	36
Formaldehyde	11.5	2.0×10^2	11	7.3

Sparkleen (a lab glass cleaning agent) as a dentrifrice in limited test-
ing. Additional testing is necessary if conclusive results are to be
obtained.

B. Etching Reagents

From prior studies it was found that conditioning or etching agents
affected the Ag deposit. Poole and Johnson had observed that acid
etchants (formic, lactic, and hydrochloric) preferentially dissolved the
axial portions of the prism heads whereas EDTA preferentially dissolved
the peripheral regions of the prisms. Accordingly, the etching behavior
of H_3PO_4 and EDTA were examined separately and in combination. The
results show that EDTA etching, independent of, or in combination with
H_3PO_4, makes no significant difference in the resistance of the deposit
when N_2H_4 is used as the reducing agent. When $FeSO_4$ and $Fe(NH_4)_2(SO_4)_2$
were used as reducing agents, the results appeared unfavorable to EDTA.
However, a larger number of samples need to be examined. Nevertheless,
when hydrazine is used as the reducing agent, EDTA appears to be as
effective an etchant as 42.5 wt.% or 21.25 wt.% H_3PO_4.

Table II lists the average resistance of Ag-plated tooth enamel for
three etchants as a function of the pH of the AgF solution with N_2H_4 as
the reducing agent. No definite correlation is observed. Sodium
fluoride and ammonium fluoride were used as etching agents for surface
enamel also and they appear to be promising candidates. Preliminary
results are shown in Figs. 1 and 2. They appear to be comparable to the
standard H_3PO_4 etch on the basis of the conductance of the deposit.
Figs. 1 and 2 also show the effect of the pH of the silver solution on
the resistance. When $FeSO_4$ is used as the reductant, the optimum pH of
the silver solution appears to be in the intermediate range, whereas
for N_2H_4 the resistance is lower when the pH is high.

Fig. 1 Average resistance of Ag plated tooth enamel as a function of
the pH of $AgNO_3$ solution and the etching agent. The sequence
of operation was: glycerin, saline, $NaHCO_3$, saline, WB,
NaF/NH_4F etch for 60 sec., WB, 100 gpl $AgNO_3$ + HNO_3 or NH_4OH –
10 mlpl N_2H_4 (pH = 9·4), 5X. (*The teeth used at 11·5 pH were
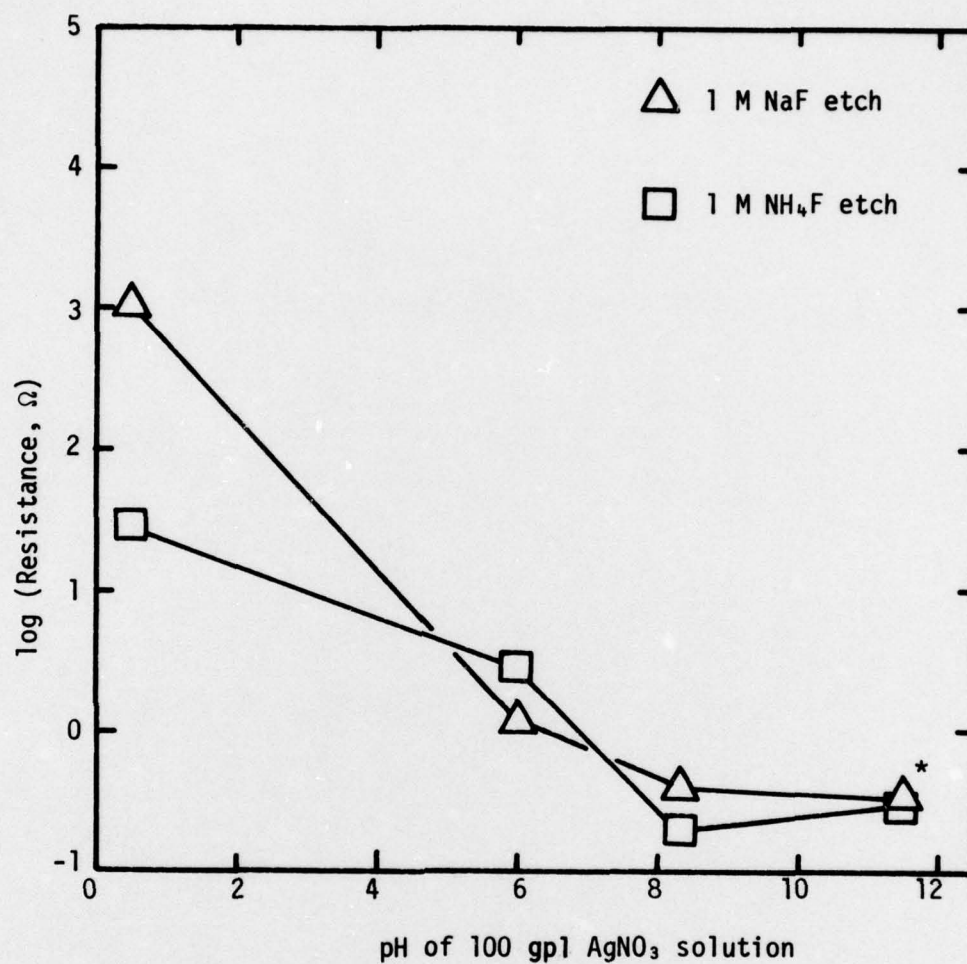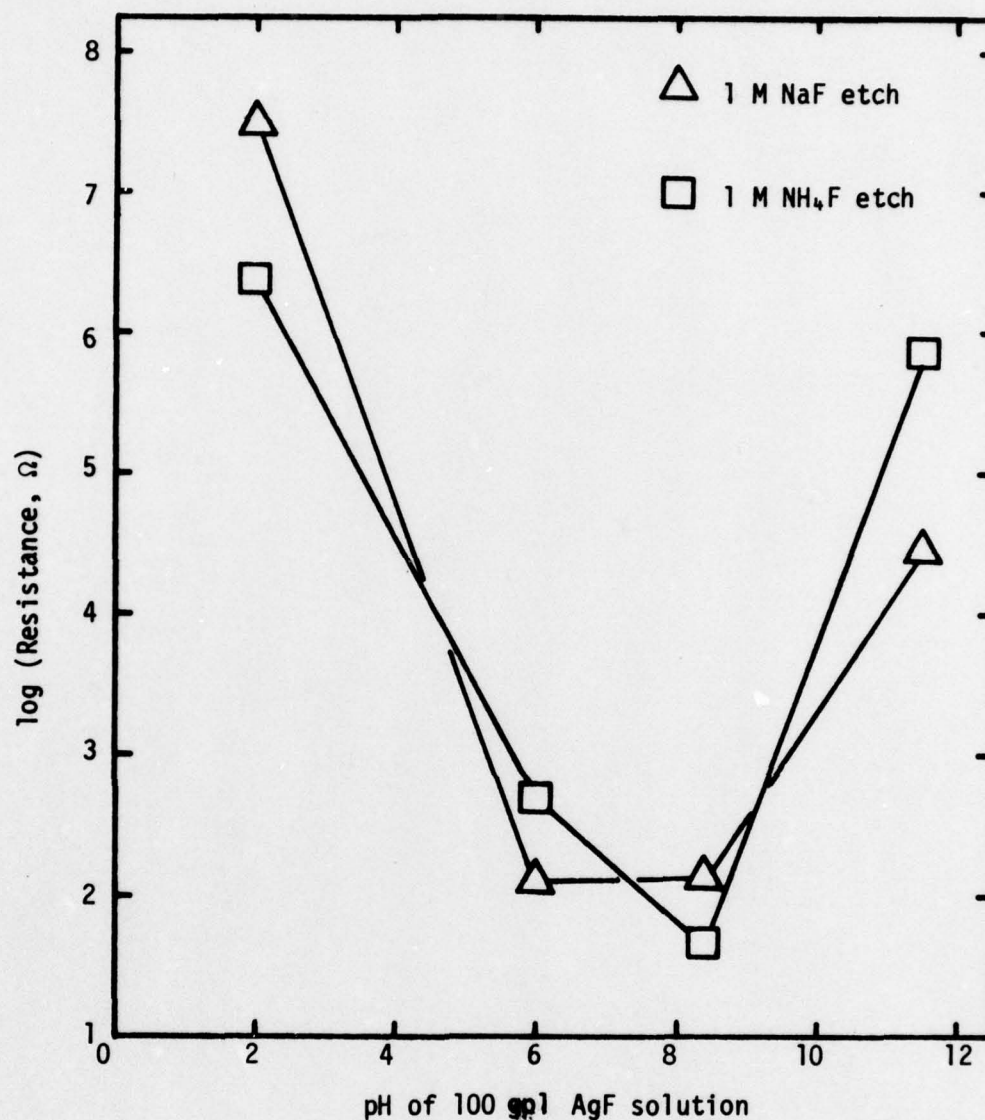stored in formaldehyde.)

Fig. 2   Average resistance of Ag plated tooth enamel as a function of the
pH of AgF solution and the etching agent. The sequence of
operation was: formaldehyde, $NaHCO_3$, saline, WB, NaF/NH_4F etch
for 60 sec., WB, 100 gpl AgF + HNO_3 or NH_4OH - 400 gpl $FeSO_4 \cdot 7H_2O$
(pH = 6 with NH_4OH), 10X.

Reversing the usual sequence of the Ag solution - reducing agent application showed no significant differences in the conductance of the Ag deposit on tooth enamel when five applications were made, Table III.

However, the treatment used between successive applications has some influence on the resulting Ag deposit. If the deposit is washed with water between the applications, a part of the Ag is lost resulting in a film with a higher resistance than an unwashed deposit. The amount of Ag washed away depends on the severity of the wash and also on the residence time allowed for the Ag deposit to adhere to the surface.

The results for other etching agents studied as alternates for the standard 42.5% H_3PO_4 are shown for both $AgNO_3$ and AgF solutions in Figs. 3 and 4 respectively. From the resistance data, the 2.4 M NH_4F, 3% H_2O_2, 10% H_2O_2, 8.5% H_3PO_4 and 21.25% H_3PO_4 appear to be comparable to 42.5% H_3PO_4, although the optimum pH of the AgF solution shifts (Fig. 4). However, the preliminary tests where the deposit was washed with water after one or two applications indicated that the 42.5% H_3PO_4 was a better etchant than the 10% H_2O_2 or 2.4 M NH_4F since the former still had an adherent black layer and the latter did not. So it appears that adherence testing will be a better way for evaluating the etchants.

C. Alternate Reducing Agents

Various reducing agents were used for both AgF and $AgNO_3$ solutions in an attempt to find a reductant that would produce better or equivalent deposits obtained with hydrazine or ferrous sulfate. Alternate reducing agents tested were ferrous ammonium sulfate, FeF_2, $FeCl_2$, SnF_2, $SnSO_4$, CoF_2, $CoSO_4$, H_2O_2, glucose, dextrose, and hydroquinone. The results of these tests are shown in Tables IV and V.

TABLE III

Effect of reversing the usual sequence of applying Ag solution and reducing agent on the resistance (Ω) of Ag plated tooth enamel. The sequence of operation was: formaldehyde storage, Sparkleen scrub, 0.9% saline, WB, etch for 60 sec., WB, Ag solution/reducing agent - reducing agent/Ag solution (5X).

Sequence	Etchant		
	21.25 % H_3PO_4, Ω	42.5 % H_3PO_4, Ω	1.0 M HCl, Ω
100 gpl AgF (pH=11.5 with NH_4OH) - 10 mlpl N_2H_4	2	2.7	4.5
10 mlpl N_2H_4 - 100 gpl AgF (pH=11.5 with NH_4OH)	13	9.7	14
100 gpl AgF (pH=11.5 with NH_4OH) - 10 mlpl N_2H_4	21 [a]	13 [a]	-
10 mlpl N_2H_4 - 100 gpl AgF (pH=11.5 with NH_4OH)	2.2[a]	2.6[a]	-
100 gpl $AgNO_3$ (pH=10 with NH_4OH) - 10 mlpl N_2H_4	15	5	70
10 mlpl N_2H_4-100 gpl $AgNO_3$ (pH= 10 with NH_4OH)	20	1.5	300

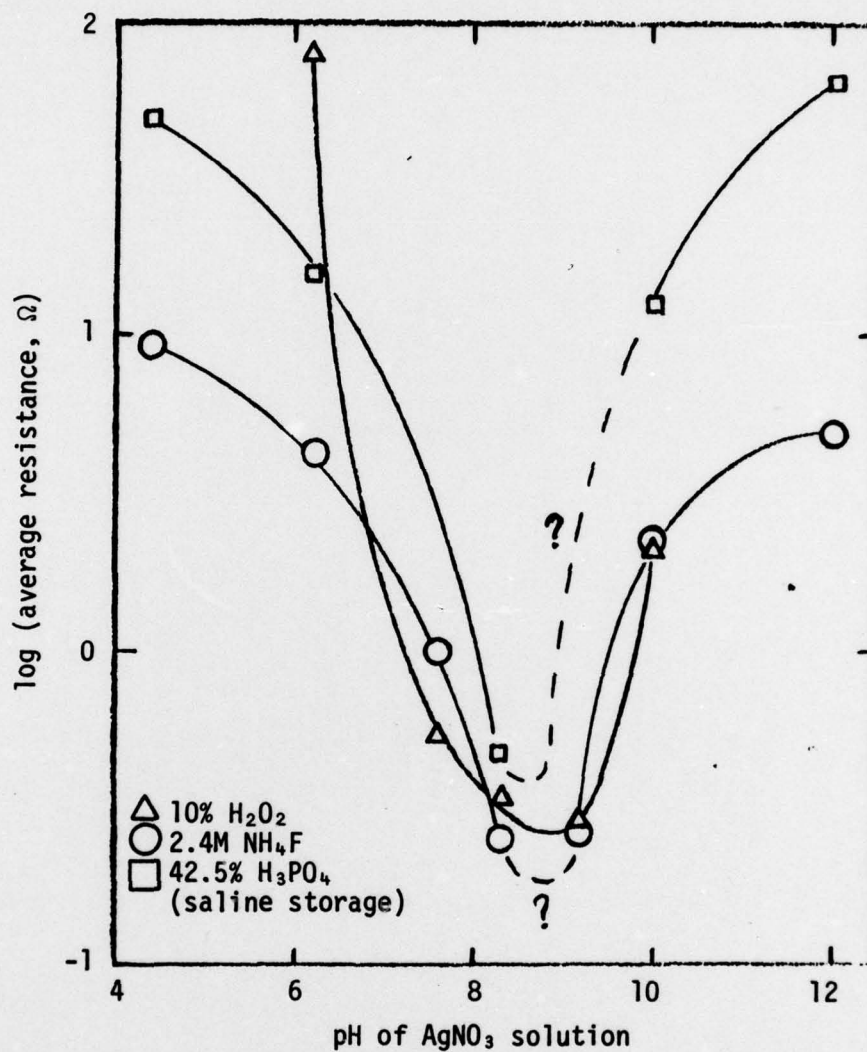a. The tooth was washed between successive applications

Figure 3. Average resistance of silver deposit on ivory as function of the pH of AgNO₃ solution and etching agents. [Plating sequence: etch, WB, 100 g/l AgNO₃ + HNO₃ or NH₄OH - 400 g/l glucose + 1.0M NaOH (12.1 pH), 10X.]
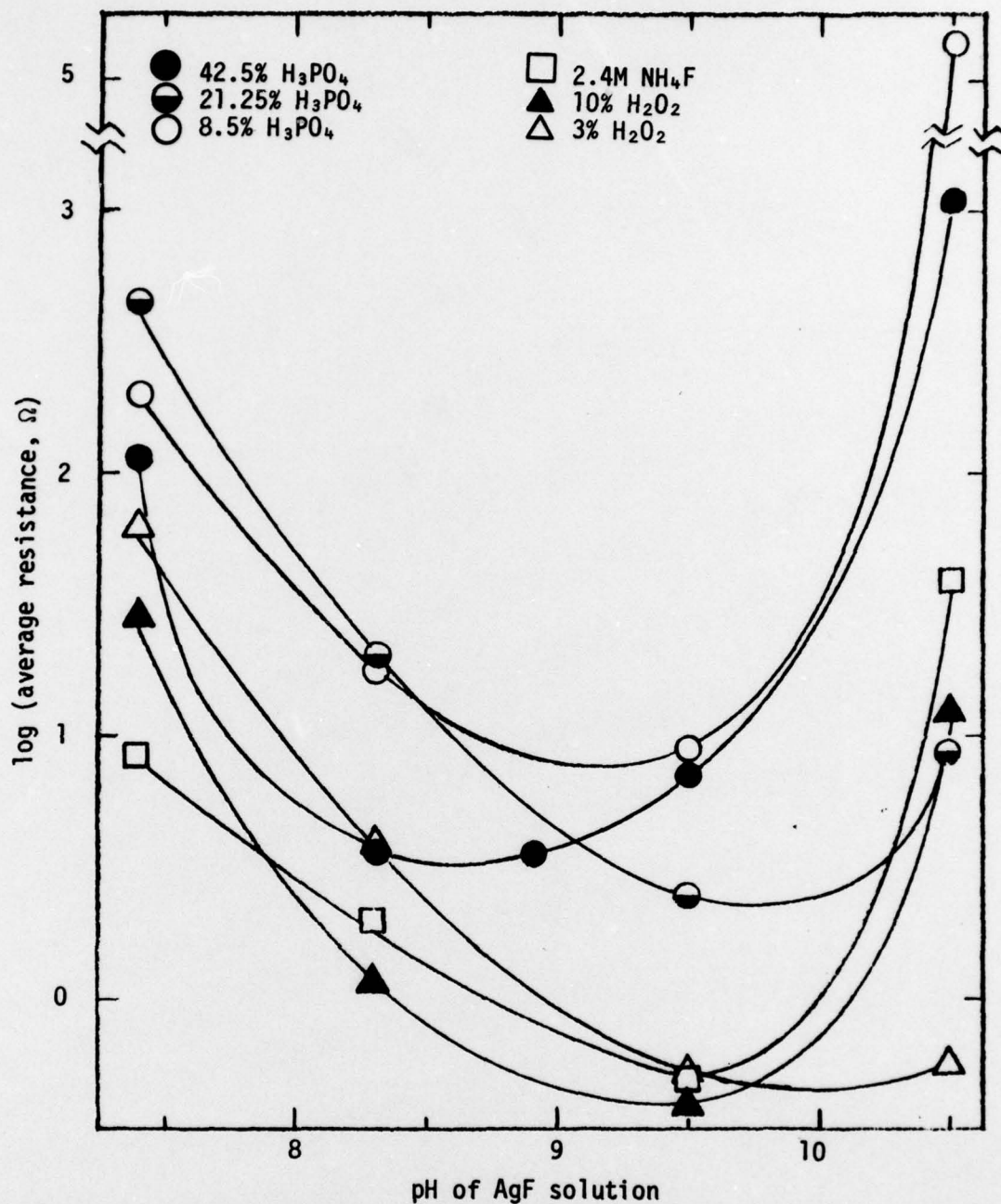
Figure 4. Average resistance of the silver deposit on ivory as a function of the pH of AgF solution and etching agents. [Plating sequence: etch, WB, 100 g/l AgF + NH₄OH - 400 g/l glucose + 0.5M NaOH (pH=11.6), 10X.]

TABLE IV

Average resistance values of the Ag plated tooth enamel as a function of the reducing agent and the pH of the AgF solution. The sequence of operation was: glycerin storage, water wash, $NaHCO_3$ scrub, water wash, saline solution, WB, 42.5% H_3PO_4 etch for 60 sec., WB, AgF - reducing agent (10 X). The residence time between successive applications was the usual 30 sec. unless otherwise noted.

Reducing Agent	100 gpl AgF solution		
	pH = 0.5 with HNO_3 Ω	pH = 7.4 Ω	pH = 8.3 with NH_4OH Ω
Saturated SnF_2 (pH=2.6)	4.0×10^{3a}	5.3×10^{3a}	1.5×10^{5a}
Saturated $SnSO_4$ (pH=1.6)	5.9×10^{4a}	9.9×10^{2a}	7.4×10^{6a}
Saturated FeF_2 (pH=4.2)	7.4×10^{7a}	7.9×10^{7a}	4.0×10^{7a}
400 gpl Dextrose (pH=4.7)	∞^b	∞^b	∞^b
Saturated Dextrose (pH=4.7)	$> 10^{7a,b}$	-	-
Saturated CoF_2 (pH=5.5)	1.9×10^{7c}	1.2×10^{8c}	∞^c
280 gpl $CoSo_4 \cdot 7H_2O$ (pH=3.2)	1.3×10^{6a}	7.5×10^{3a}	∞^a
Saturated hydroquinone (pH=3.8)	5.0×10^{7c}	24^c	0.4^c
10% H_2O_2 (pH=3.9)	-	∞^d	$> 10^{7d}$
Saturated $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	-	5.5	-

a. 5 minute intervals between applications

b. 5 applications

c. formaldehyde storage

d. saline storage

TABLE V

Average resistance values of the Ag plated tooth enamel as a function of the reducing agent and the pH of the $AgNO_3$ solution. The sequence of operation was: glycerin storage, water wash, $NaHCO_3$ scrub, water wash, saline solution, WB, 42·5% H_3PO_4 etch for 60 sec., WB, $AgNO_3$ - reducing agent (10X). The residence time between successive applications was the usual 30 sec. unless otherwise noted.

Reducing Agent	100 gpl $AgNO_3$		
	pH = 0·5 with HNO_3 Ω	pH = 6·2 Ω	pH = 8·3 with NH_4OH Ω
Saturated SnF_2 (pH=2·6)	$2·9 \times 10^{7a}$, ∞^a	$3·7 \times 10^{7a}$	∞^b
Saturated $SnSO_4$ (pH=1·6)	$1·9 \times 10^{7b}$	$1·9 \times 10^{7b}$	$1·8 \times 10^{7b}$
Saturated FeF_2 (pH=4·2)	$3·0 \times 10^{7a}$	∞^a	$3·2 \times 10^{7b}$
400 gpl $FeCl_2·4H_2O$ (pH=0.9)	∞^a, $8·9 \times 10^{7a}$	$8·6 \times 10^{7a}$	-
400 gpl $FeSO_4·7H_2O$ (pH=3·3)	∞^a	48^a	-
400 gpl $FeSO_4·7H_2O$ (pH=5·5 with NH_4OH)	-	$1·3 \times 10^{2b,c}$	-
Saturated CoF_2 (pH=5·5)	$1·5 \times 10^{7c}$	$8·8 \times 10^{7c}$	$1·1 \times 10^{8c}$
280 gpl $CoSO_4·7H_2O$ (pH=3·2)	$1·7 \times 10^{7b,c}$	∞, $1·2 \times 10^{8b,c}$	$4·4 \times 10^{7b,c}$
400 gpl Dextrose (pH=4·7)	∞^a	∞^a	∞^a
400 gpl Glucose (pH=4·8)	∞^a	∞^a	$1·5 \times 10^{7a,b}$
Saturated hydroquinone (pH=3·8)	$1·0 \times 10^{5c}$	$1·4 \times 10^{5c}$	$0·5^c$
10% H_2O_2 (pH=3·9)	$8·9 \times 10^{7d}$	$7·3 \times 10^{7d}$	$9·8 \times 10^{7d}$

a. 5 applications

b. 5 minute intervals between applications

c. formaldehyde storage

d. saline storage

Dextrose and glucose are particularly slow acting and the resulting Ag deposits have very high resistances. A residence time of 5 min. was used in most tests (although impractical in actual practice) to see if the reducing agents were capable of producing a good quality deposit given sufficient time to reduce the Ag^+ to Ag. $SnSO_4$, and SnF_2 appear to be effective on the basis of conductance.

As indicated above, the sugars (glucose, dextrose, and sorbitol - a sugar derivative) by themselves gave resistance values of $\sim10^8\Omega$ or greater. If an activator is applied as a third solution, the deposit becomes shiny and has a gold-like appearance with a typical resistance of about 1Ω. The activator consisted of 180 g/l NaOH and 78 ml/l NH_4OH with a pH > 14. It was felt that a pH greater than 14 would be too severe for use in clinical practice and accordingly attempts were made to lower it or find alternatives. The average resistance values (Ω) are given in Table VI as a function of the activating solutions and pH of the $AgNO_3$ solution and are quite encouraging.

From the results it appears that the pH of the activating solution is very critical to deposit conductivity. However, with 14.8 M NH_4OH (pH = 13.4) as an activator, the deposits are not as good as those obtained from using 4.5 M (NaOH (pH > 14) probably due to the formation of complex ions with silver. Also, generally, the higher the pH of the $AgNO_3$ solution (tested up to 8.3 pH) the better were the conductances.

Since a three solution system is more complicated the activator was added directly to the reducing agent with good results. The average resistance values (Ω) are given in Table VII as a function of the addi-tives to the reducing agent and the pH of the $AgNO_3$ solution. Here again the pH of the combined solution was critical. It seems that a reductant pH of about 11.6 or higher is necessary to obtain good

TABLE VI

Average resistance values (Ω) of the Ag plated ivory as a function of the activating solution and pH of the $AgNO_3$ solution. The sequence of operation was: saline storage, wash, $NaHCO_3$ scrub, saline solution, WB, 42.5% H_3PO_4 etch for 60 sec., WB, 100 g/l $AgNO_3$ + (HNO_3 or NH_4OH) - 400 g/l glucose (pH = 4.75) - activating solution, 10X. The residence time between successive applications was 30 sec.

Activating Solutions	pH of $AgNO_3$ Solution			
	0.5	6.2	8.3	10
4.5M NaOH + 78 ml/l NH_4OH (pH>14)	1.4×10^2	0.3	0.3	--
14.8M NH_4OH (pH=13.4)	1.6×10^7	6.0×10^6	4.9×10^6	--
4.5M NaOH (pH>14)	4.1	--	0.7	--
78 ml/l NH_4OH + ~40 g/l $NaHCO_3$ (pH=9.9)	9.5×10^6	6.4×10^7	8.1×10^7	--
.01M NaOH (pH=11.6)	7.0×10^6	3.9×10^6	3.5×10^6[a]	--
4.5M NaOH + 78 ml/l NH_4OH (pH>14)	2.7[a,b] 1.8[b,c]	--	--	0.2 [b]
1.12M NaOH + 19.5 ml/l NH_4OH (pH=13)	--	--	--	1.6×10^5[b]

a. Only one sample was tested.

b. Reducing agent was sorbitol, and substrate was human tooth enamel.

c. The sequence of application was: $AgNO_3$ - activator - reducing agent.

TABLE VII

Average resistance values of the Ag plated ivory as a function of additive to the reducing agent. The sequence of operation was: saline storage, water wash, NaHCO$_3$ scrub, water wash, saline solution, WB, 42.5% H$_3$PO$_4$ etch for 60 sec., WB, 100 g/1 AgNO$_3$ - 400 g/1 glucose solution + additive (10X). The residence time between successive applications was 30 sec.

Additives	pH of AgNO$_3$ Solution								
	.5 Ω	2.5 Ω	4.4 Ω	6.2 Ω	7.6 Ω	8.3 Ω	9.2 Ω	10 Ω	12 Ω
1.9M NH$_4$OH (pH=10.8)	1.3×10^7	--	--	2.9×10^7	--	1.8×10^7	--	--	--
2.65M NaOH (pH=13.2)	4.1×10^1	2.2×10^1	--	2.7	--	3.1×10^{-1}	--	6.4	4.3
1.0M NaOH (pH=12.1)	--	--	4.5×10^1	1.7×10^1	--	4.7×10^{-1}	--	1.4×10^1	5.8×10^1
1.0M NaOH (pH=12.1)[a,b]	--	--	9.3	4.2	1.0	2.5×10^{-1}	2.7×10^{-1}	2.2	4.9
1.0M NaOH (pH=12.1)[a,c]	--	--	--	7.0×10^1	5.4×10^{-1}	3.4×10^{-1}	2.8×10^{-1}	2.1	--
0.1M NaOH (pH=10.6)	--	--	3.0×10^7	1.3×10^7	--	1.4×10^4	--	1.2×10^8	2.8×10^7

a. Stored in glycerin.

b. 2.4M NH$_4$F etch.

c. 10% H$_2$O$_2$ etch.

deposits. With regard to the $AgNO_3$ solution, intermediate pH's produced better deposits than either low or high pH's. The scanning electron microscopy revealed that the particle size of the deposits decreased with increasing pH of the silver solution. The effect of some other additives on the resistance of Ag plated ivory is shown in Table VIII. The inclusion of formaldehyde increased the resistance and the addition of NH_4OH did not seem to have any beneficial effect. SEM micrographs of some of these deposits are shown in Fig. 5.

Even though the pH of the reducing solution may be prohibitively high, the results were very encouraging. As seen from the figures the deposits are very dense and continuous and compare favorably with those obtained using hydrazine as the reductant. This strongly indicates that changes in the chemical parameters or the use of additives may be an effective method to improve existing systems, such as the iron sulfate.

The activating solution - 180 g/l $NaOH$ and 78 ml/l NH_4OH - was also used with the reducing agents SnF_2 and $SnSO_4$. It was hoped that the high pH of activating solution would produce stannate ions which are strong reductants. As shown in Fig. 6, the resistances of the deposits obtained with the use of the activator were better than those without it. Tests were also done in which the activator was added to the reductant to make it a two solution system. As shown in Fig. 7 the resistance of the deposits decreases with increasing pH of $AgNO_3$ solution up to 8.5 pH. With further increase in the pH the resistance increases. $SnSO_4$ appears to be a better reductant than SnF_2. (Also in the earlier tests it was found that $FeSO_4$ was better than FeF_2.) Further experimentation seems warranted to optimize the pH of the activator solution or search for alternate activators with Sn^{+2} as the reducing

TABLE VIII

Average resistance of Ag plated ivory as a function of additions to the glucose reducing agent. [Plating sequence: 2.4M NH_4F etch for 60 sec., WB, 100 g/l AgF + NH_4OH (pH=8.3) - 400 g/l glucose + additive* (pH∿10.6), 10X.]
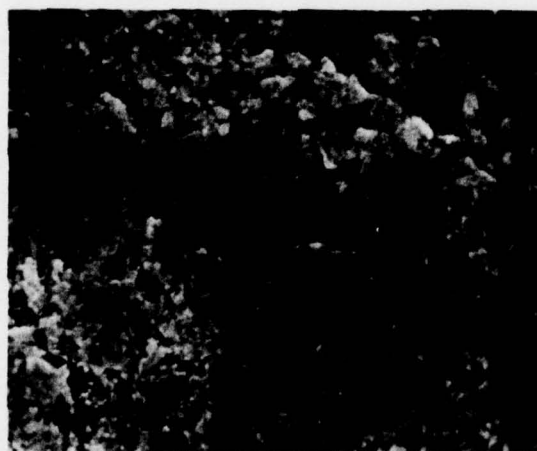
*Additives	Average Resistance (Ω)
0.1M NaOH (pH=10.6)	3.7
0.1M NaOH + 1.7 ml/l NH_4OH (pH=10.8)	8.4
0.1M NaOH + 2 ml/l formaldehyde (pH=10.6)	110
0.1M NaOH + 2 ml/l formaldehyde + 1.7 ml/l NH_4OH (pH=10.6)	21

a

b

c

Fig. 5. Surface morphology of Ag deposited on ivory. NH_4F etch; $AgNO_3$ (pH varied) 100 gpl; Glucose + NaOH (12.1 pH) 400 gpl; 10 repetitions, 3000X. $AgNO_3$ pH.
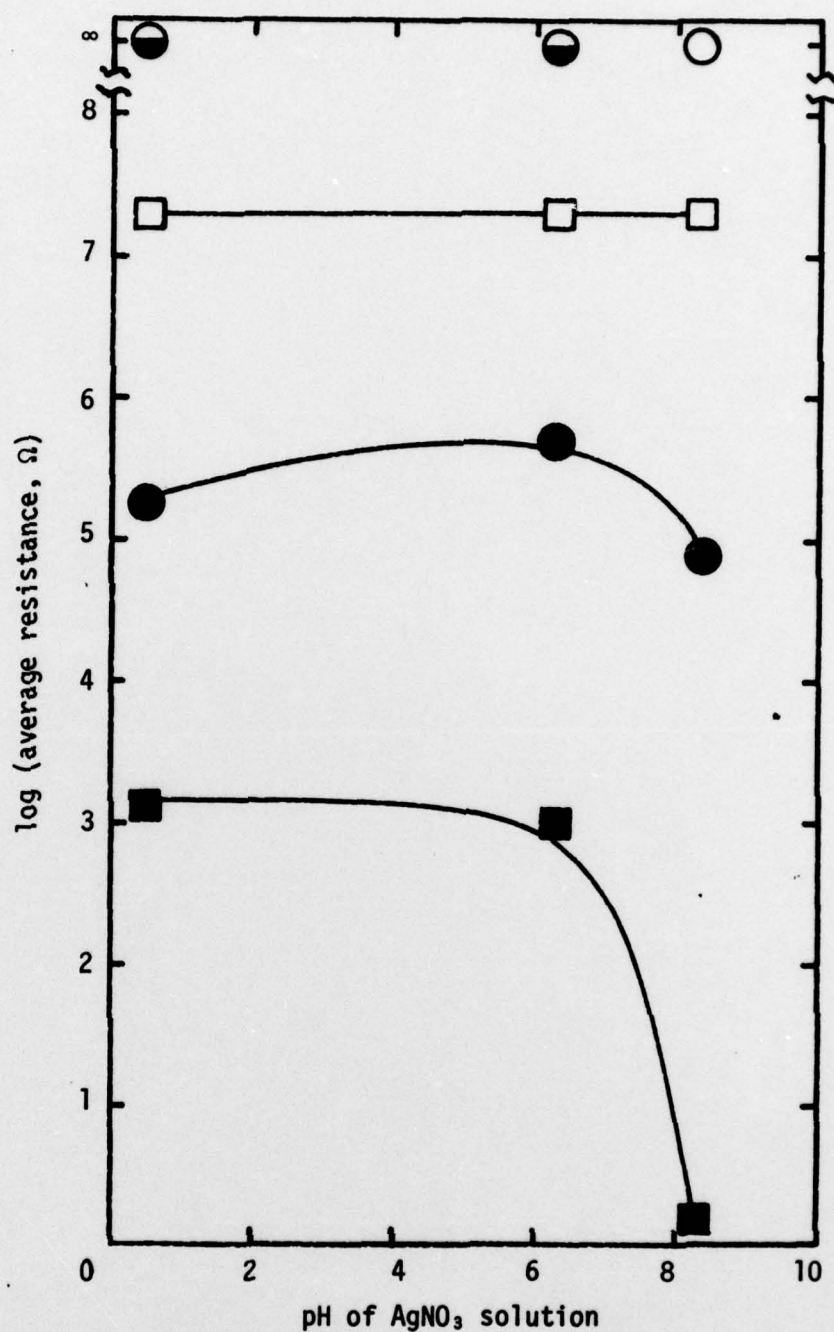
a. 4.4   b. 8.3   c. 12

Figure 6. Effect of activator (180 g/l NaOH + 78 ml/l NH$_4$OH) on the resistance of the silver deposit as a function of the pH of AgNO$_3$ solution. (Plating sequence: 42.5% H$_3$PO$_4$ etch, WB, 100 g/l AgNO$_3$ + HNO$_3$ or NH$_4$OH - SnF$_2$ or SnSO$_4$, 10X.) (◑ - teeth, sat. SnF$_2$, 5X; ○ - teeth, sat. SnF$_2$, 5 min. res. time; □ - teeth, sat. SnSO$_4$, 5 min. res. time; ● - ivory, sat. SnF$_2$ - activator; ■ - ivory, sat. SnSO$_4$ - activator.)
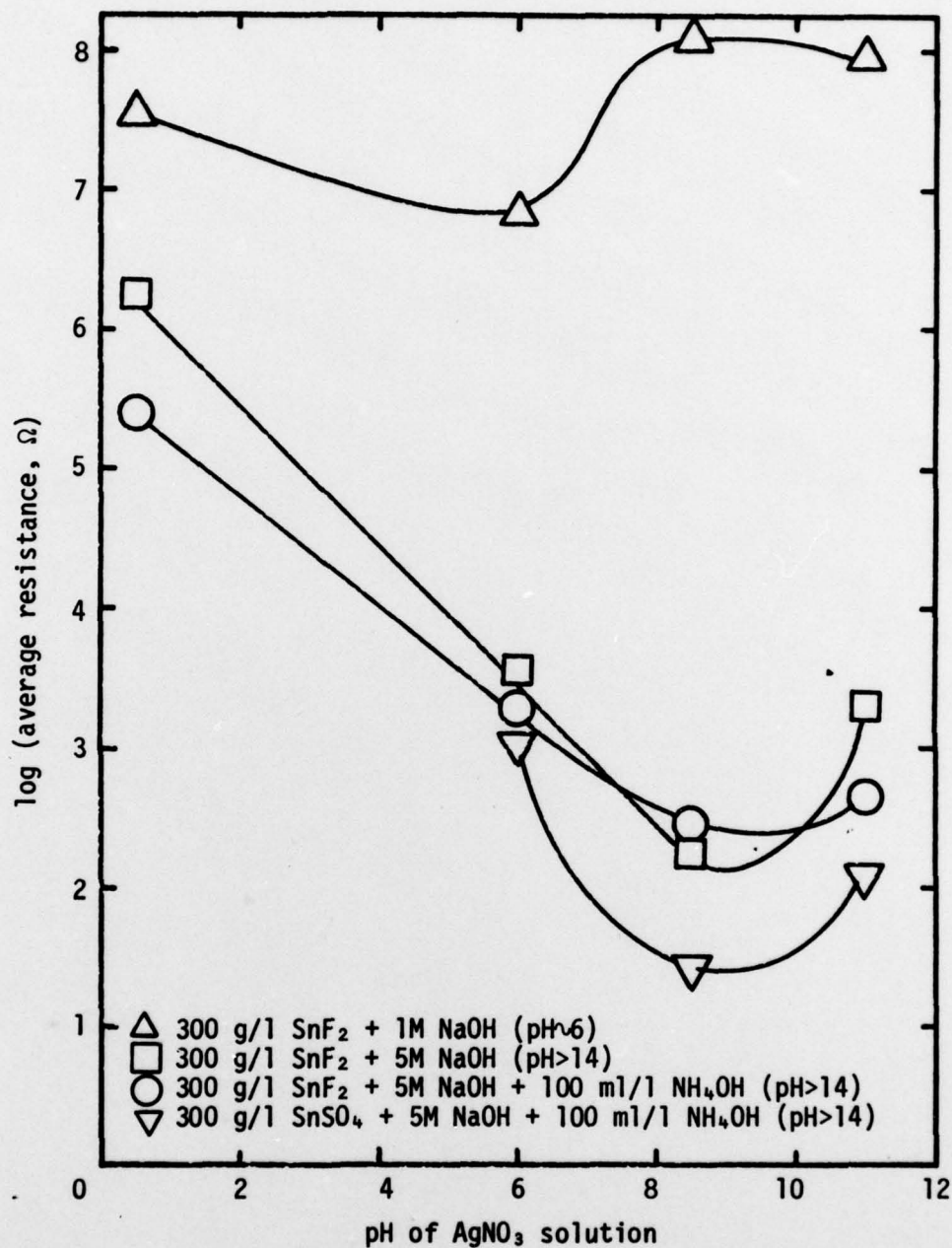
Figure 7. Effect of activator additions (to the reducing agent) on the resistance of the silver deposited ivory as a function of the pH of $AgNO_3$ solution. (Plating sequence: 42.5% H_3PO_4 etch, WB, 100 g/l $AgNO_3$ + HNO_3 or NH_4OH - reducing agent, 10X.)

agent. Attempts to use $CoSO_4 \cdot 7H_2O$ (pH = 6.5 with NaOH or NH_4OH) as a reducing agent were not successful.

As reported earlier, saturated hydroquinone produced excellent results as a reductant. Since hydroquinone is toxic, tests were made at a much lower concentration (10 g/l), which produced deposits with resistances of about 30Ω.

D. Rate Studies

Preliminary rate studies have been conducted with AgF-glucose system to determine the amount of Ag deposited as a function of the glucose concentration. A fixed area of the ivory was plated and then the deposit was dissolved in HNO_3 and analyzed by the atomic absorption technique. The results are given in Table IX. The concentration of NaOH in the reductant was varied to keep a constant pH. It can be seen from the table that the rate of Ag deposition increases sharply up to ∿20 g/l glucose concentration, and then only gradually beyond ∿20 g/l glucose. From these preliminary tests, the rate of Ag^+ reduction with glucose is comparable to that of reduction with $FeSO_4$. More tests will be conducted to obtain the optimum parameters.

E. Metal Additions

Since nucleation sites influence the rate of a reaction, some experiments were conducted to study the effect of readily available nuclei on the deposits. Additions of Fe^{++}, Cu dust, Zn dust or CuCl powder, in small concentrations, were made to the $AgNO_3$ solution. The solution was kept in an ultrasonics bath for about 5 minutes in order to avoid growing large particles. Also, it is believed that the number of nuclei produced is probably proportional to the amount of a particular additive. The resistances of the deposits obtained in this manner are plotted against the concentration of the addition agent in Fig. 8. There is a

TABLE IX

Average amount of Ag deposited on ivory as a function of the concentration of the reducing agent. [Plating sequence: 42.5% H_3PO_4 etch, WB, 100 g/l AgF + NH_4OH (pH=9.5) – glucose + NaOH, 10X.]

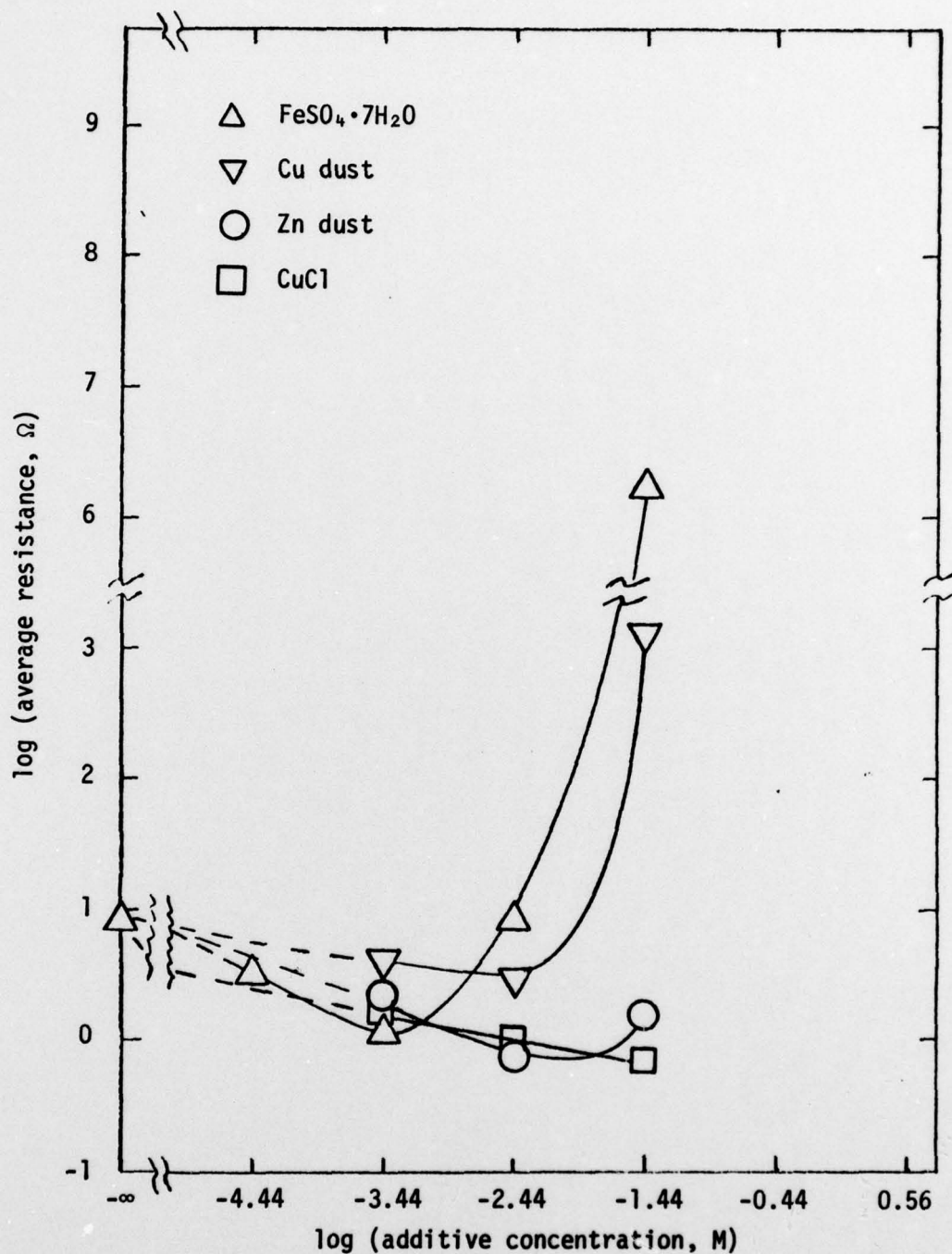| Concentration of Glucose (g/l) pH~11.7	Ag (mg/cm^2)
1.0	1.0
10	0.9
20	1.6
50	1.5
100	1.5
200	1.5
400	1.7
600	1.7
800	1.5

Figure 8. Average resistance of the silver deposit on ivory as a function of the additives (to $AgNO_3$) and their concentration. [Plating sequence: 42.5% H_3PO_4 etch, WB, 100 g/l $AgNO_3$ + additive (pH~6) - 400 g/l $FeSO_4$ (pH~6), 10X.]

slight reduction in the resistance initially but as the concentration of the addition agent increases, the resistance starts increasing. However, this did not happen with CuCl addition up to the range tested. It appears that probably there is an optimum number of nuclei which the system will bear. Also, the size of the nuclei could be important. It would be interesting to see what effects these addition agents would have on the adherence of the deposits. From the morphological studies it appears that in the case of $FeSO_4$ additions, the deposit with the least resistance is the deposit which is well packed and dense.

F. X-ray Studies

In the earlier work the black layer appearing after the first one or two applications of AgF-hydrazine sequence on the tooth or the ivory substrate was presumed to be silver. The x-ray studies confirmed this. Also, the yellow coloration appearing on the substrate after applying the silver solution was found to be Ag_3PO_4 by x-rays.

As the conductance of a deposit increases one would expect the coverage of the surface with Ag to increase. This condition was verified for the system AgF-glucose by plotting the ratio of the intensities of the strongest peaks of hydroxyapatite to silver (I_{HAP}/I_{Ag}) against the pH of the AgF solution (see Fig. 9). These plots resemble the resistance profiles of Fig. 8 in that the minima of I_{HAP}/I_{Ag} and the resistance occur in the intermediate pH region.
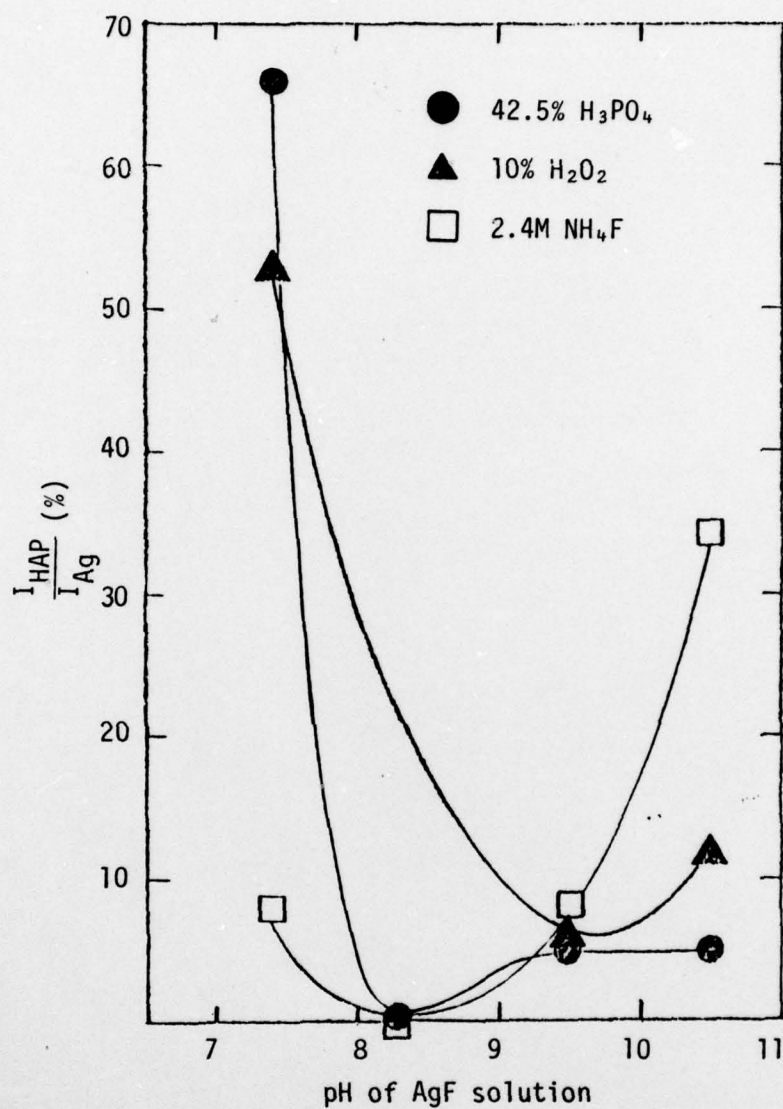
Figure 9. Surface coverage of ivory ($\frac{I_{HAP}}{I_{Ag}}$) as a function of the pH of AgF solution and etching agents. The number of applications was 10 with 400 g/l glucose + 0.5M NaOH (pH=11.6) as the reducing agent.

III. CONCLUSIONS

Overall progress in last year's research has been good. Glycerin storage for extracted teeth is better than formaldehyde. The resistance data indicate that the dentrifrice used to cleanse the teeth influences the deposit. The etching agents used also influence the metal films. However, wash tests indicated that some of these etching agents produce loose deposits. Shear testing of films would be a better way to evaluate the etching agents. But these etching agents could possibly be used in conjunction with H_3PO_4 to alter the surface properties of the teeth. Sugars and Sn^{+2}/Sn^{+4} couple were found as alternate reducing agents. However, they seem to work best at high pH's. Morphological studies indicate that by adjusting the pH of Ag solutions or by using addition agents in Ag solution dense deposits could be obtained.

Experimental results indicate that the system chemistry is very important in determining the nature of the deposit obtained. Solution pH seems to be one of the most critical parameters and this must be studied more extensively. Increased efforts must also be made to find a means of densifying the deposit and minimizing its porosity. It has been shown that the grain size and distribution changed substantially with Ag solution pH. Attempts will be made to conduct similar studies using the Fe reducing system to see if this trend is duplicated. The use of Chemical additives, both organic and inorganic, will also be studied. Another area that will be investigated will be the chemistry of the phases formed during the first repetition of the process. X-ray analysis has revealed the presence of Ag_3PO_4. It is not known if this

phase is integrated into the phosphate structure of the hydroxyapatite, but if so, then the possibilities for chemical bonding may be enhanced. In general, more work is needed to characterize the surface during the initial phases of film formation, as this is probably the key to strength adherence and protective qualities ultimately obtained.

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